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Monolayers of Dicetyl Fumarate and Dicetyl Maleate, and Their Interaction with Bromine and Iodine

Leon J. Shereshefsky Howard University

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MONOLAYERS OF DICETYL FUMARATE AND DICETYL MALEATE, AND THEIR INTERACTION WITH BROMINE AND IODINE

By J. L. Shereshefsky

Chemistry Department, Howard University, Washington, D. C.

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This paper presents studies of surface pressure and surface potentials of monolayers of dicetyl maleate and dicetyl fumarate. The stability of these monolayers is considered from the point of view of the orientation of the polar groups in the head-group of the monolayer. It includes data and discussion of a stable double film of the fumarate ester. There are also presented data on the effect of bromine, iodine and acidified iodides on the potentials of both types of monolayers. The lowering of the potentials of the maleate ester monolayers and the absence of this effect in the fumarate monolayers, is explained on the basis of the presence of a strongly polar interface at the maleate monolayer, and the lack of such an interface at the fumarate monolayer, and that the polar interface induces polarization in the adsorbate molecules. Secondly, the polarized molecules in being absorbed at the interface assume an orientation which reduces the surface potentials of the monolayers. The paper also contains data and discussion on the relation of the lowering effect to the concentration of the reagent.

The presence of a double bond with its different stereochemical configurations in the hydrocarbon chains affects many of the properties of monolayers. Thus, a double bond in the middle of the chain causes the film to expand at a lower temperature than films with saturated chains of equal number of carbon atoms. The same is true, but to a lesser extent, when a double bond is adjacent to the carboxyl group. A double bond in the hydrocarbon chain effects an increase in the limiting area, the surface potential and dipole moment.

The effect of a double bond in the head group on the stability of the monolayer recently was shown[1] to depend on its geometrical configuration. Dilauryl maleate forms stable liquid expanded films, while its *trans* isomer, the fumarate, tends to form unstable films of the liquid condensed type.

The present paper is a further study of this property, and shows that the stereochemical configurations of the double bond in the head of the monolayer determine in part the orientation of the molecule in the monolayer, affect the vertical component of the apparent dipole moment and influence the interaction of halogens and halides with the monolayer.

Experimental

Apparatus.—The film balance was a Langmuir type described previously.[1] The surface potentials were deter-

(1) J. L. Shereshefsky and A. A. Wall, *J. Am. Chem. Soc.*, **66**, 1072 (1944).

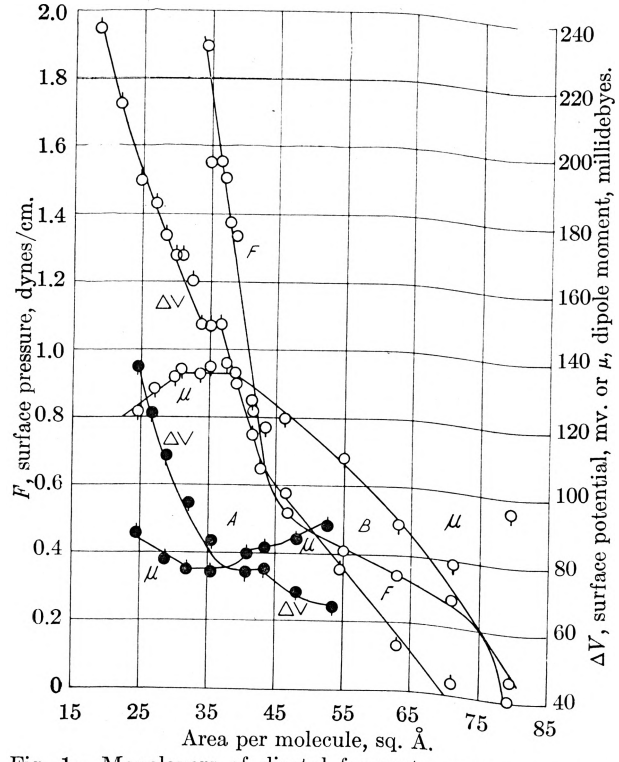

Fig. 1.—Monolayers of dicetyl fumarate at 20°: A, low potential monolayer; B, intermediate potential monolayer.

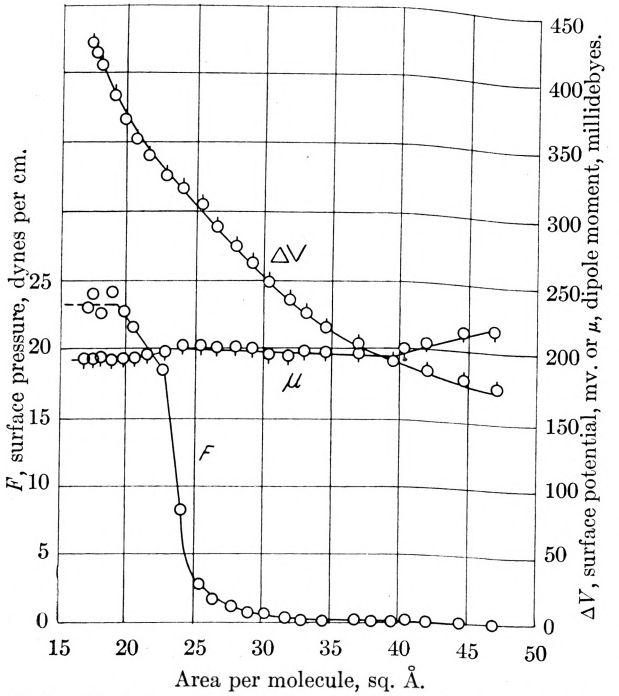

Fig. 2.—High potential monolayer of dicetyl fumarate at 20°.

mined with a polonium air-electrode and a Lindemann electrometer. The air-electrode was held in an arm capable of movement over the whole surface of the film. The balance, electrodes and electrometer were enclosed in an earthed metal-clad box. The electrometer needle was projected through a microscope on a screen outside the enclosure. The movement of the movable barrier and of the air-electrode arm were effected from outside the box; the tension of the wire holding the float was similarly adjusted from outside the box.

The films were spread from an "Agla" syringe[1] with a precision of 0.0002 cc. The solvent of the spreading solutions was a petroleum ether fraction boiling between 60 and 80°.

Monolayers.—The monolayers were the dibasic cetyl esters of maleic and fumaric acids.

The dicetyl fumarate was prepared from cetyl alcohol, m.p. 50–51°, and fumaric acid, by digesting an excess of the former with a small quantity of the latter at 140°, in the presence of a few drops of concd. sulfuric acid, until most of the solid fumaric acid reacted. The cooled mixture was dissolved in benzene, the sulfuric acid removed with solid barium hydroxide, and the solution dried with anhydrous sodium carbonate. The solids were removed by filtration, and the benzene was distilled off. The product was crystallized several times from ethyl alcohol until the crystalline material melted sharply at 58.5°. Crystals of this material when melted on a watch-glass give a clear and colorless melt. When the crystals are melted in a saturated alcohol solution a light brown liquid is obtained. After separation and solidification this substance shows the same m.p. as the white crystals.

Dicetyl maleate was prepared from cetyl alcohol and maleic acid, in a similar manner, except that the digestion was carried out at 60° for a much longer period. The reaction was much slower and the yield only 70%. Repeated crystallization from ethyl alcohol gave needle-like crystals melting at 42.5°. On melting, this substance goes over into another form with a lower m.p. of 38.5°. On recrystallization the original crystalline form is obtained.

The substrates were 0.01 *N* hydrochloric, 0.01 *N* sulfuric acid, solutions of bromine and iodine of several concentrations and solutions of sodium and potassium iodide of several concentrations. The halogen and halide solutions were either in 0.01 *N* hydrochloric or 0.01 *N* sulfuric acid.

Experimental Results and Discussion

Monolayers of the Fumarate Ester.—Dicetyl fumarate appears to form condensed films of two characteristic areas. In the low pressure region, the film has a low surface potential of about 150 millivolts and a limiting molecular area of 47 sq. Å., and a maximum pressure of about 2 dynes per cm. (Fig. 1). On further compression, the film seems to behave as if it were collapsing as shown by point B on the F and ΔV curves, but on careful compression carried out in small steps, the monolayer behaves like a homogeneous phase. The bend in the surface pressure–area curve occurs at about 0.6 dyne and 45 sq. Å. per molecule. The surface potential–area curve shows similar behavior: the potential, first rises slowly with compression and then rises more steeply when beyond 42.5 sq. Å. The changes in the vertical component of the apparent dipole moment, μ, indicate that orientation of the molecules is continually increasing until the molecular area is compressed to about 40 sq. Å. Beyond this point further compression has a very slight effect on the dipole moment. This low pressure film was obtained on 0.01 *N* hydrochloric and sulfuric acids.

The other form of the fumarate film, shown in Fig. 2, appears to have a limiting area of about 25–26 sq. Å. per molecule, and withstands pressures up to 22–23 dynes per cm. It is formed when the film exhibits high surface potentials, even at large molecular areas. In these films the surface potential continually increases with compression, showing a change of phase at about 25 sq. Å. However, the vertical component of the dipole moment slowly decreases with compression, until a molecular area of about 40 sq. Å. is reached, indicating changes in the orientation of the molecules in the film. From this point to about 23 sq.

Å. the dipole moment appears to remain constant, but seems to fall with further compression until the film collapses.

Films also were obtained which showed very low surface potentials and which were very fragile, collapsing at pressures of 0.5 dyne per cm. These films exhibited potentials of about 65 millivolts at a molecular area of 40 sq. Å. They were obtained both on hydrochloric and sulfuric acids. ΔV and μ *vs.* area diagrams for these films on sulfuric acids are shown in Fig. 1.

Orientation of Fumarate Ester.—The complex behavior of the fumarate ester monolayers is undoubtedly related to the structure of the head-group of the film. This part of the monolayer includes the rigid carbon–carbon double bond group and two flexible ester groups. The freedom of rotation of each of the ester groups with respect to the rigid C=C group, and the internal rotational freedom within each ester group around the ether oxygen and the carbon atoms in the ether group endow the head-group with many possible orientations in the monolayer. Each of these orientations will have characteristic vertical components of the moment and surface potentials.

One of these orientations, Fig. 3A, is where the ester groups are in transposition with respect to the C=C group, and together with the latter are flat on the surface with the hydrocarbon chains in *trans*-positions and tilted away from the surface. This configuration occupies an area of about 58 sq. Å. per head-group. The first signs of a positive pressure in the low potential monolayer appear at about this area.

When the CH_2– group adjacent to the ether oxygen in each ester group is flat on the surface, the potential and vertical component of the dipole moment are zero. When this is inclined to the surface with an angle a, the vertical component of the moment is 1.14 cos 110 sin a, where 1.14 is the R–O bond moment, 110 is the bond angle. Taking the dielectric constant of the surface as 7, the angle a as 90°, in both chains, the vertical component of the dipole moment at its maximum is about 110 millidebye. This corresponds approximately to the moment for the monolayer on hydrochloric acid at 47 sq. Å., Fig. 1. The calculated area for this configuration, taking into consideration the cross-section of the long hydrocarbon chains and the width of the head-group is 46.5 sq. Å. per molecule.

The high pressure monolayer is very likely a double monolayer, where a single monolayer of the above configuration is superimposed on another, in series. The factors in favor of this view are, first, the fact that the observed dipole moment is approximately twice the calculated value for the single monolayer, and, second, the apparent partial collapse of the monolayer as demonstrated at point B, Fig. 1.

In the heterogeneous film which obtains at molecular areas larger than 45–50 sq. Å., areas of high potentials frequently were observed, side by side, with areas of low potential. This is in agreement with the above view of the complexity and flexibility of the orientations of the head-group of these monolayers.

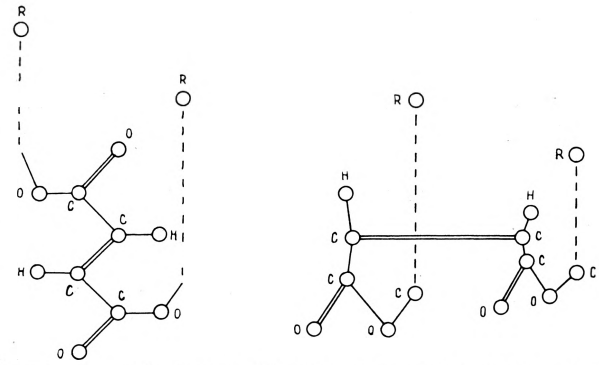

Fig. 3.—Orientation of head group in the monolayers of dicetyl maleate and fumarate: A, dicetyl fumarate; B, dicetyl maleate.

The Effect of Halogens and Halides on Fumarate Monolayers.—Monolayers of the fumaric acid ester were spread on neutral and acidified bromine, iodine and potassium iodide solutions of different concentrations. These monolayers, a few minutes after spreading, were compressed to a fixed molecular area or pressure, and the surface potential measured at frequent time-intervals, until approximate constancy of values.

With the exception of 0.01 N H_2SO_4 as substrate, in which case a lowering was observed, the potentials of the monolayers tended to rise continually over an interval of about 15 to 45 minutes, before reaching a constant value. A summary of the observations is given in Table I.

TABLE I

SURFACE POTENTIALS OF DICETYL FUMARATE ON DIFFERENT SUBSTRATES

Substrate		Area per molec., sq. Å.	Potential, mv.	Dipole moment, millidebye
Acid	Halogen or halide			
0.01 N HCl	.....	40	190	195
0.02 N HCl	.....	40	218	208
0.10 N HCl	.....	44.7	66	78
	6.8×10^{-6} N, I_2	40.8	244	264
0.01 N HCl	1.7×10^{-5} N, I_2	38	250	254
0.01 N HCl	3.4×10^{-5} N, I_2	38	254	257
0.01 N HCl	5.1×10^{-5} N, I_2	38	239	241
0.01 N HCl	1×10^{-3} N, KI	39.6	209	220
0.01 N H_2SO_4	.....	40.0	75	75
0.01 N H_2SO_4	3.4×10^{-5} N, I_2	40.0	106	112
0.01 N H_2SO_4	1×10^{-3} N, KI	40.0	10	10
0.01 N H_2SO_4	1×10^{-3} N, KI	38.2	73	75
0.01 N H_2SO_4	5×10^{-3} N KI	38	50	50
0.01 N H_2SO_4	2.3×10^{-3} N, Br_2	39.7	96	99
0.01 N H_2SO_4	2.3×10^{-3} N, Br_2	51.2	0	0
0.01 N H_2SO_4	4.5×10^{-3} N, Br_2	49.6	10	13

It is to be noted that iodine showed a tendency to increase the potential of the monolayer, whether it was acidified with hydrochloric or sulfuric acid. Bromine showed a similar effect at a molecular area of 40 sq. Å. and the opposite effect at about 50 sq. Å. Potassium iodide in sulfuric acid effected a decrease in the potential, the change increasing with concentration of substrate and molecular area. These effects, however, were not sufficiently pronounced to be quantitatively significant.

Monolayers of the Maleate Ester.—This ester

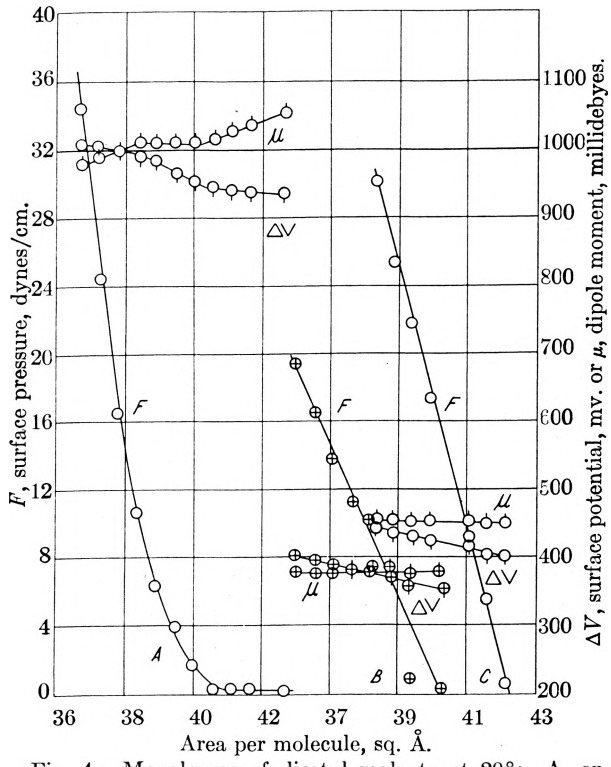

Fig. 4.—Monolayers of dicetyl maleate at 20°: A, on 0.01 *N* HCl; B, on 0.01 *N* HCl + 0.001 *N* NaI; C, on 0.01 *N* HCl + 0.001 *N* NaI + 0.0002 *N* I_2.

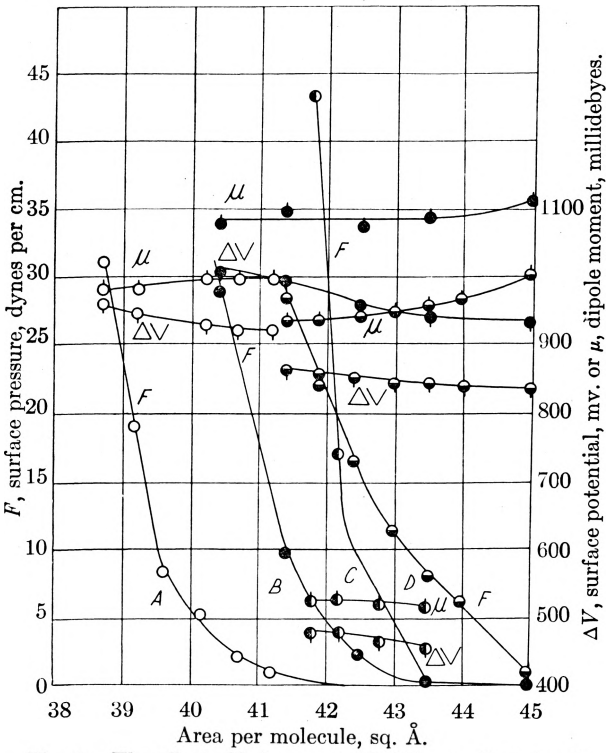

Fig. 5.—The effect of halogens and halides on dicetyl maleate monolayers: A, 0.005 *N* KI + 0.01 *N* H_2SO_4; B, 0.01 *N* H_2SO_4; C, 0.0004 *N* I_2 + 0.001 *N* KI + 0.01 *N* H_2SO_4; D, 0.0045 *N* Br_2 + 0.01 *N* H_2SO_4.

forms a condensed film with a limiting molecular area of 38.8 sq. Å. on 0.01 *N* HCl. At the higher extension of about 42 sq. Å., the film exhibited jel-like properties, in that it oscillated, when disturbed by an air blast; below 39 sq. A., it was rigid, and displayed no oscillation, when similarly disturbed. The film displayed high stability, as no signs of collapse were noticeable at a surface pressure of 43 dynes per cm., the highest pressure conveniently observed (Fig. 4.). On sulfuric acid of the same normality the film appears of even greater stability and larger limiting molecular area, 41.8 sq. Å., as shown in Fig. 5.

The surface potentials are very high, perhaps the highest ever observed for saturated hydrocarbon chains. They were somewhat higher on sulfuric acid than on hydrochloric acid. The same is true for the vertical component of the dipole moments. The μ–A curves show that compression beyond the limiting molecular area caused a distortion of the dipoles in the head-group of monolayers spread on hydrochloric acid. The fact that this does not occur in the monolayer on sulfuric acid points to greater stability of the monolayer.

Orientation of the Maleate Ester.—The mutual repulsion of the two carbonyl oxygens and the adhesional forces between the long hydrocarbon chains require that the ester groups in the head-group of the molecule orient themselves in *cis*-position, so that one is the mirror image of the other, as shown in Fig. 3B. This orientation, using the accepted bond moments and angles[2] and 7 for the value of the dielectric constant, gives a vertical component of 930 millidebye per molecule. The observed values at the limiting area are 1010 on hydrochloric acid and 1090 on sulfuric acid. Closer agreement between observed and calculated values here and for the fumarate ester is perhaps dependent on the value taken for the dielectric constants.

The Effect of Several Reagents on the Maleate Monolayer.—In Table II are summarized the effects of several different reagents on the surface potential of the maleate monolayer. It will be noted that on hydrochloric acid the equilibrium potential of the monolayer is established almost immediately, while on sulfuric acid and non-acidified sodium iodide this potential is established only after the lapse of some time. On these substrates, the potentials are initially low, and reach the equilibrium values after 50 or 60 minutes.

This, in light of the reduced potentials obtained on sodium and potassium iodides acidified with hydrochloric acid, suggests that the initial low potentials were due to the adsorption of hydrogen iodide in the case of sodium iodide, and the hydrosulfate ion in the case of sulfuric acid. These substances are highly polar and would tend to be adsorbed with the hydrogen toward the substrate, since the monolayer dipole is positive toward the hydrocarbon chain. The slow rise of the potential that follows the initial lowering is perhaps due to the formation of the Helmholtz-double layer by the adsorption of the iodide and sulfate ions.

In the case of potassium iodide substrate acidified with sulfuric acid, the potential is initially only slightly lower than the equilibrium potential on sul-

(2) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, p. 307.

TABLE II

THE EFFECT OF SEVERAL REAGENTS ON THE SURFACE POTENTIAL OF DICETYL MALEATE MONOLAYERS

Time, min. / Substrate	Millivolts 0[b]	20	40	50	∞	Area, sq. Å./molec.	Pressure, dynes/cm.
0.01 *N* HCl + 4.5×10^{-4} *N*, Br_2	(952)	947	941		935[c]	40.5–41.1	0.46
0.01 *N* HCl + 2.25×10^{-3} *N*, Br_2	(941)	921	902	892	882[c]	39.4–40.8	3.96
0.01 *N* HCl + 4.5×10^{-3} *N*, Br_2	(975)	922	870	845	795[c]	42–44	3.76
0.01 *N* H_2SO_4 + 2.25×10^{-3} *N*, Br_2	(904)	894	883	877	871[c]	51.2	0.10
0.01 *N* H_2SO_4 + 4.5×10^{-3} *N*, Br_2	(864)	841	817	805	797[c]	51.3	0.18
0.01 *N* HCl + 3.4×10^{-5} *N*, I_2	(650)	734	738	728		39.9–40.2	2.48
0.01 *N* HCl + 3.4×10^{-5} *N*, I_2	(670)	752	750	744		41.0	0.46
0.01 *N* HCl + 5.1×10^{-5} *N*, I_2	(574)	694	706	708		41.0	0.28
0.01 *N* HCl + 3.4×10^{-4} *N*, I_2	444				444	42.4–43.5	.64
0.001 NaI	(730)	844[a]	894	904	904	40.5–39.4	.18
0.01 *N* HCl + 0.001 *N* NaI	(310)	355	365	367	368	39.4–40.3	.18
0.01 *N* HCl + 0.001 *N* KI	428				428	40.0	.10
0.01 *N* HCl + 0.001 *N* NaI + 2×10^{-4} *N*, I_2	(310)	342[a]	353	359	370	40.6–42.2	.46
0.01 *N* HCl + 0.015 *N KI* + 3×10^{-3} *N*, I_2	(46)	57[a]	63	66	69	40.7–40.3	.37
0.01 *N* H_2SO_4 + 0.001 *N* KI	(964)	956	948	942	934	41.2–42.7	.18
0.01 *N* H_2SO_4 + 0.005 *N* KI	(938)	930	924	920	912	40.6–41.2	.92
0.01 *N* H_2SO_4 + 0.001 *N* KI + 4×10^{-6} *N*, I_2	(850)	906[a]	931	934	934	42.2–42.6	.46
0.01 *N* H_2SO_4 + 0.001 *N* KI + 4×10^{-4} *N*, I_2	(340)	406[a]	422	431	455	42.3–43.5	.37
0.01 *N* H_2SO_4 + 0.005 *N* KI + 2×10^{-4} *N*, I_2	(386)	434[a]	452	452	452	42.4	.10
0.01 *N* H_2SO_4	(670)	865[a]	898	910	914	51.8	.09
0.01 *N* HCl	917				917	60.3	.09

[a] Time sequence: 10, 20, 30. [b] Extrapolated values in parentheses. [c] At 60 min.

furic acid alone. The further slow decrease is very likely due to adsorption of hydrogen iodide which is in competition with the hydrosulfate ion.

Bromine in hydrochloric and sulfuric acid substrates lowers the potentials of the monolayer. The lowering is proportional to the concentration, and the rate of lowering per unit concentration is approximately a constant. In the case of the hydrochloric acid substrate this rate constant, $\Delta\Delta V/c\Delta t$, as obtained from the data in Table II, is approximately 550, 450 and 620 millivolts per minute per mole for the bromine concentrations of 0.45, 2.25 and 4.5 millimoles per liter, respectively. In sulfuric acid as substrate, the rate constant in the two concentrations studied is 223 millivolts per minute per mole, approximately one-half of the former value. Whether this halved efficiency is related to the displacement of or counteraction to the doubly charged sulfate ion, as against the chloride ion, is an interesting question.

The effect of iodine on the surface potentials of the maleate monolayers is similar to that of bromine. However, the lowering is greater and takes place very much faster. Contrary to the behavior of bromine, the potential in the case of iodine is reduced almost instantaneously, and then builds up slowly to a low equilibrium value. Due to this behavior it is not possible to evaluate the rate constant, for the lowering effect. The lowering, however, seems to be proportional to the logarithm of the concentration.

The greatest lowering of approximately 870 millivolts was obtained by the action of iodine in the presence of acidified 0.005 *N* potassium iodide.

In Figs. 4 and 5 are shown diagrams of surface pressure *vs.* molecular area of four monolayers, after their surface potentials have been reduced from 100 to 600 millivolts. It will be noted that all of them show limiting molecular areas ranging from 40.2 to 43.8. Yet, none of them show signs resembling collapse under the relatively high pressure to which they are subjected. Their limiting molecular areas are different, their compressibilities are different, but in general they resemble the parent monolayer. This is convincing evidence that no transformation to the *trans* isomer has taken place.

The changes in the surface potentials and in the apparent dipole moments evidently are due not to the rearrangement of the relative position of the dipoles in the head-group, but to the adsorption of the hydrogen iodide, the iodine, or the bromine. Yet, the same dipoles are present in the head-group of the fumarate molecule, and no such effects were observed in the monolayer formed by this substance.

Furthermore, bromine and iodine are symmetrical molecules, and have no dipole moments associated with them. How, then, do they affect by adsorption a reduction in the surface potential of the monolayer?

To answer these questions, it would seem necessary to assume, first, that the presence of individual dipoles are not sufficient, and that to effect adsorption the dipoles must be oriented so that the interface is strongly polar, as in the case of the dicetyl maleate monolayer. Secondly, the polar interface must induce polarization in the molecules prior to their being adsorbed. Only when in this polarized state can the surface potential be affected by adsorption. In this connection it is of interest to call attention to the catalytic effect of a polar surface on the addition of halogens to ethylene, demonstrated by Stewart and Edlung[3] and Norrish.[4]

The author wishes to take this belated opportunity of expressing his appreciation and indebted-

(3) T. D. Stewart and K. R. Edlung, *J. Am. Chem. Soc.*, **45**, 1014 (1923).

(4) R. G. W. Norrish, *J. Chem. Soc.*, **123**, 3006 (1923).

ness to Sir Eric Rideal for the hospitality and helpfulness in connection with his brief stay at the Colloid Science Laboratory at the Cambridge University.